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STRUCTURE FORMATION OF PORCELAIN BASED ON NONTRADITIONAL RAW MATERIALS WITH A BIOLOGICALLY ACTIVE ADDITIVE

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The mechanism of the reaction between the components of porcelain mixtures based on Gusevskoe stone in the presence of molasses additive with a comprehensive effect is analyzed. The possibility of using this additive as an environmentally pure strengthening additive to produce porcelain articles by single firing on the basis of nontraditional materials is demonstrated.

Factories in the Far East use nontraditional types of materials for porcelain production, namely, Gusevskoe stone (dacite porphyry) and Chalganovskoe quartz-feldspar sand in the form of products of its concentration, i.e., kaolin and feldspar.

These raw materials differ in their genesis and chemico-mineralogical composition from the materials traditionally used. Their mineral composition contains nearly all components required for the production of porcelain. Thus, porcelain stone from the Gusevskoe deposit contains kaolinite (14.5–38.5%); quartz (52.8–58.2%); mixed-layer mineral of the rectorite type characterized by alternating layers of montmorillonite and hydromica packets (2.8–30.1%); hydromica and plagioclase in small quantities; and impurity minerals such as rutile, pyrite, limonite, leucoxene, ore, and ore dust [1]. It should be taken into account that porcelain stone used as material are of the alkali-free varieties and normal-alkalinity varieties with a limited content of colorant oxides (Fe_2O_3 , TiO_2).

It is established [2] that pegmatite quartz has a higher reactivity in high-temperature firing than quartz sand. Quartz contained in the Gusevskoe stone dissolves much more actively than pegmatite quartz, hence the lowering of energy barriers in the process of formation of the ceramic material structure. This is due to the fact that each quartz grain in pegmatite or Gusevskoe stone, as a consequence of long-time physical and chemical natural effects, has a relatively lower strength and a higher crack content on the surface than quartz contained in feldspar.

The next type of nontraditional material is Chalganovskoe kaolin. Its mineral composition does not differ significantly from the Prosyankovskoe kaolin used in porcelain production: the main mineral is kaolinite, but there are grains of

calcium carbonate, quartz, rutile, and a silicate of the chlorite type [1]. These kaolins are similar in their content of the main oxides. However, Chalganovskoe kaolin has a somewhat higher content of iron oxides, which is outside the limit of the state standard requirements.

A very specific material is white-burning Troshkovskoe clay mined in the Irkutsk Region. It differs from plastic clay traditionally used in the porcelain-faience industry in that it does not swell in water and has a lower content of iron and titanium oxides. Troshkovskoe clay consists of kaolinite and montmorillonite. As was seen in the chemical analysis of the material performed by the central laboratory of the Vladivostok Porcelain Factory, clay from the Troshkovskoe deposit has an increased content of oxides of alkaline and alkaline-earth metals (2.57%). The content of the specified oxides in clays from the Latnenskoe deposit traditionally used in the porcelain industry is 1.85%.

The study of the production of porcelain based on a mixture of raw materials from the Far East [3] established that as a result of the lower activation energy values, all processes of porcelain formation are more active at a lower temperature. A typical porcelain structure is formed already at a temperature of 1200°C. It is represented by glass and primary and secondary mullite, whereas pure highly fused and tridimittized quartz grains are found very rarely.

The compulsory replacement of high-quality materials previously used in the porcelain industry in the Primorie Region (in particular, Prosyankovskoe kaolin and Veselovskoe clay) by local materials (Chalganovskoe kaolin, Troshkovskoe clay) resulted in decreased mechanical strength of intermediate molded products in the air-dried state and, consequently, an increase in the technological waste up to 13%. Accordingly, the unit produced cost increased.

It should be noted that manufacturers of porcelainware now try to decrease the wall thickness. At the same time, the

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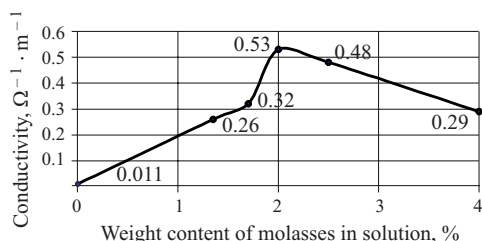


Fig. 1. Electric conductivity of solution as a function of the molasses content.

sensitivity of molded intermediate product to mechanical impacts grows. Therefore the problem of increasing the strength of porcelain material in the air-dried state has become topical.

It is known that the strength of porcelain mixture in the air-dried state depends on the mixture composition (especially on the content of argillaceous components), the type of clay and kaolin used, the type and size of grains of stony materials, the methods for preparing and storing mixtures, the molding method, the degree of dryness, and packing density of particles.

To increase the strength of intermediate air-dried porcelain made of porcelain mixtures based on nontraditional Far East raw materials, a strengthening additive was introduced into the mixture in the form of a natural complex of biologically active compounds, namely, molasses, which is waste generated by the local sugar industry. The proposed method makes it possible not only to increase the mechanical strength of air-dried intermediate product to the values typical of porcelain product after a first firing at 850°C, but also to significantly shorten the duration of milling of the porcelain mixture to a required dispersion (according to the technology accepted in production of porcelain the residue on a No. 0056 sieve should be 1.2 – 1.3%). Furthermore, the use of this method does not cause unnecessary shrinkage and makes it possible to preserve the open porosity needed for glazing of articles.

Analysis of experimental data [4] suggests that the use of additive in the amount of 1.35% has a substantial positive effect. Thus, the duration of milling of the experimental mixture decreased from 5 h to 4 h 25 min compared with the industrial mixture, i.e., by 11.7%. The static bending strength of air-dried samples increases from 5.5 to 6.2 MPa, i.e., by 11.3%. This has not only decreased losses of the air-dried intermediate product in this production division but has also created conditions producing articles from this mixture with the additive by single firing.

Thus, the economic effect of the proposed method for producing porcelain mixture using molasses as a strengthening additive comes from savings in material and fuel resources, a decrease in the technological waste and rejected products, and decreased wear of machinery, and, more importantly, the method will have a beneficial effect on the environment in the region.

The performed analysis of moisture and the content of organic and inorganic components in molasses made it possible to classify this additive as a comprehensive-effect reactant acting as a surfactant (the process of milling of material components is accelerated) and an electrolyte. We investigated the correlation between the electric conductivity of molasses solution and its concentration. The conductivity of molasses solution with a mass content of molasses equal to 1.35 – 4.00% amounted to 0.26 – 0.53 $\Omega^{-1} \cdot m^{-1}$.

The shape of the curve constructed based on the experimental data (Fig. 1) confirms the theory of conductivity of electrolytes. As the concentration of the solution and, accordingly the concentration of ions increases, the conductivity grows to a certain limit. Thus, a rise of the curve is registered on the segment with a molasses content from 0 to 2 wt.%, the peak of the curve correlating with a 2% content. On further increase in the solution concentration, the conductivity decreases, which correlates with the curve decline sector.

It is interesting that the conductivity of a 1.7% solution of molasses correlates with the same value for 0.3% liquid glass solution, which is commonly used in porcelain production for making slip for casting. Thus, the obtained experimental data agree with the known dependence of the degree of dissociation of weak electrolytes on the dilution of solution [5].

Consequently, the specifics of the chemical composition of molasses have a positive effect on the mechanism of reaction between the initial components of the porcelain mixture at different stages of structure formation.

To identify the differences in the phase composition of samples made of the standard industrial mixture and the experimental mixture, we performed an analysis of their structure at the N. M. Fedorovskii All-Russia Institute of Mineral Materials using contemporary methods of physicochemical analysis. The results of x-ray phase analysis shown in Table 1 are corroborated by the data of electron microscopy of the porcelain structure of samples of both series after identical heat treatment and the data of infrared spectroscopy (Fig. 2).

The main components of materials from the industrial and experimental mixtures subjected to drying at 110°C are represented by kaolinite, quartz, and potassium feldspar with albite impurity (Table 1, Fig. 2a and b). The electron microscope study indicated that all particles contained in the experimental materials are coated by a thin organic film with mineral-phase inclusions containing metals (silicon, aluminum, potassium, etc.). The experimental sample had a higher structural homogeneity than the structure of the sample made from industrially produced porcelain. The increased degree of homogenization of the mixture components is related to using the complex additive, which could become the principal technique providing for an increase in the mechanical strength of nonfired articles. The addition of the material adsorbing on the surface of the particles of components in mill-

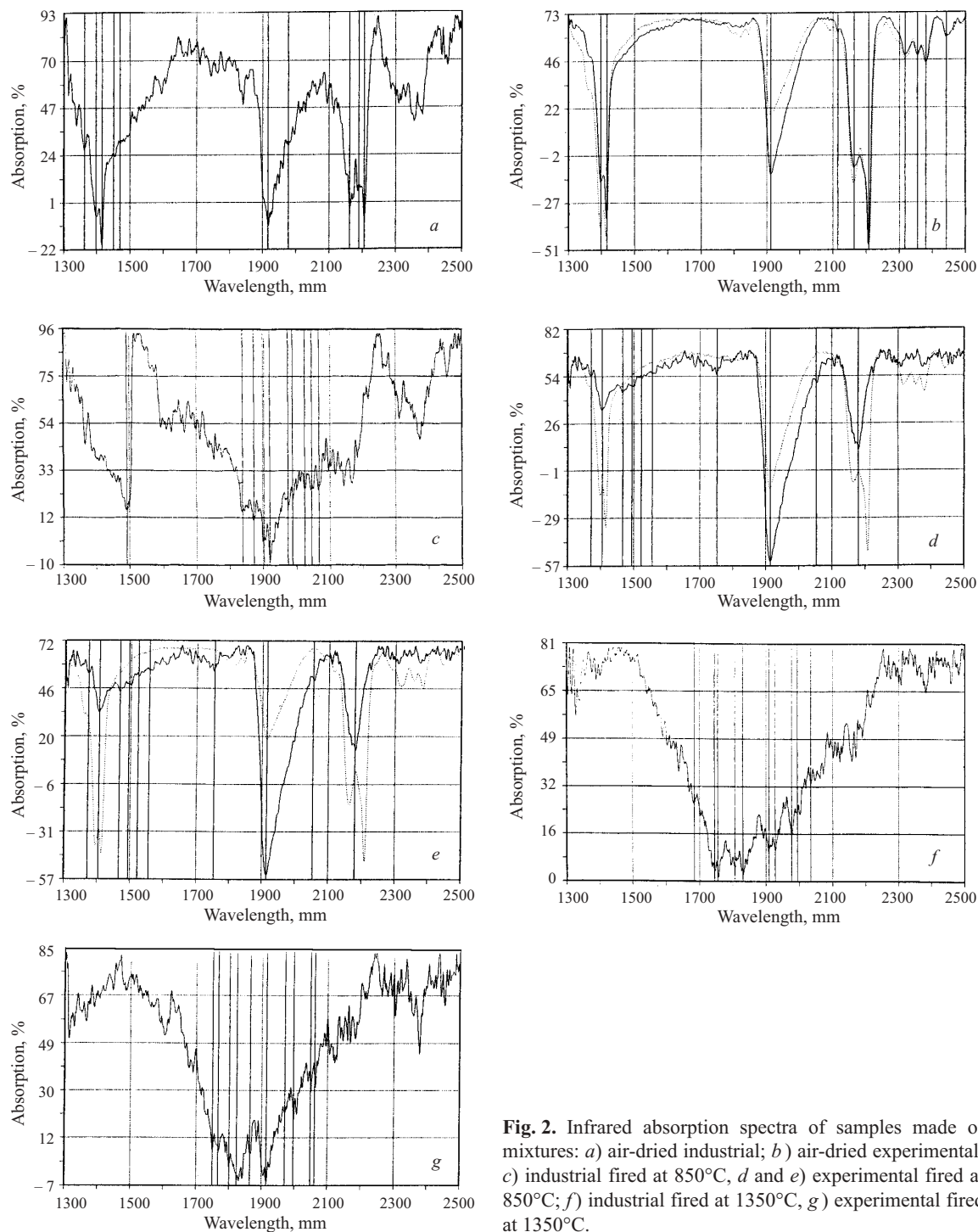


Fig. 2. Infrared absorption spectra of samples made of mixtures: *a*) air-dried industrial; *b*) air-dried experimental; *c*) industrial fired at 850°C, *d* and *e*) experimental fired at 850°C; *f*) industrial fired at 1350°C, *g*) experimental fired at 1350°C.

ing facilitates their sliding against each other and thus facilitates the formation of a dense unstressed structure.

All this indicates that the organic component of the strengthening additive acts as a flotation agent Adsorbing on chips and faces of the kaolinite particles, it neutralizes their positive charge, which increases the stability of particles and delays their thixotropic reduction. As the porcelain mixture is dried, hydrate shells of argillaceous particles are removed, and coagulation contacts transform into condensation con-

tacts (up to the formation of condensation-crystallization contacts); material is transferred via the vapor phase and precipitates on the disperse phase particles (mainly, clay components) in the form of amorphous and weakly crystalline oxide and hydroxide films that firmly fix individual particles into aggregates.

The results of x-ray phase analysis and electron microscopy of samples fired at 850°C indicate that occasional destroyed quartz grains and feldspar grain detritus are found in

TABLE 1

Sample	Treatment temperature, °C	Phase composition	
		phase	weight content, %
P-1	110	Kaolinite	40 ± 1
		Quartz	30 ± 1
		Potassium feldspar	9 ± 1
		Plagioclase (albite)	3 ± 0.5
		Hydromica	Traces
		Alunite	
		Dolomite	
		Calcite	18
		Leucite	
P-2	850	X-ray-amorphous phase	
		Quartz	28 ± 2
		Potassium feldspar	9 ± 1
		Plagioclase (albite)	~ 2.5
		Destroyed kaolinite	
		Dolomite	
		Calcite	60.5
P-3	1350	Hematite	
		Quartz	18 ± 0.5
		Mullite	28.5 ± 2
		Cristobalite	1 – 2
O-1	110	Vitreous phase	52
		Kaolinite	38.5 ± 2
		Quartz	28 ± 1
		Potassium feldspar	8 ± 1
		Plagioclase (albite)	~ 2.5
		Alunite	
		Dolomite	
		Calcite	23
		Leucite	
O-2	850	X-ray-amorphous phase	
		Quartz	27 ± 2
		Potassium feldspar	8.2 ± 0.5
		Plagioclase (albite)	2.6 ± 0.5
		Cristobalite	≤ 1
		Destroyed kaolinite	
		Dolomite	
		Calcite	~ 61
		Hematite	
O-3	1350	γ-Al ₂ O ₃ (traces)	
		Quartz	17 ± 0.5
		Mullite	28 ± 2
		Cristobalite	~ 1
		Vitreous phase	54

the mixture, corresponding to an averaged matrix with the prevailing content of primary mullite, laminar aluminosilicates, quartz, and feldspar.

The IR spectrum of the experimental sample exhibits weak absorption peaks of carbonaceous materials (Fig. 2*d* and *e*) that point to burning-out of the organic component of the strengthening additive. For a clearer picture, the IR spectra (dashed lines) of the standard kaolinite (Fig. 2*e*) and the air-dried experimental sample (Fig. 2*d*) were superimposed on the spectra of the experimental sample after the first firing.

A distinctive feature of experimental materials fired at 850°C is the presence of low concentrations of newly formed phases, i.e., amorphous kaolinite and γ-alumina (spinellide), which are not observed in the sample of the industrial mixture. It can be assumed that the presence of these phases is caused by a reaction between the strengthening additive and the nontraditional raw materials that have low energy barriers of the main structure-forming processes. Spinellide crystals in the heterogeneous structure of the emerging material can act as crystallization centers, i.e., seed for the formation of mullite crystals [6].

It was earlier established that the formation of the metakaolinite structure of porcelain materials based on Gusevskoe stone (dacite porphyry) ends at a temperature of 680°C (the temperature of the second endothermic effect). Upon a further increase in temperature up to 850°C (the first firing temperature), modification occur within the frame of the metakaolinite structure [1].

As was shown in the studies [2, 6], as the temperature increases, the solid-phase reaction of decomposition of metakaolinite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ makes it amorphous and results in its partial segregation into oxides. However, complete segregation of metakaolinite does not occur, presumably due to the difficulty of diffusion in the solid state. The products of its decomposition are spinellide $n(\gamma\text{-Al}_2\text{O}_3)$, amorphous silica $m\text{SiO}_2$, and clusters of $(1 - n)\text{Al}_2\text{O}_3 \cdot (2 - m)\text{SiO}_2$.

It is known that when the temperature exceeds the level at which condensation structures exist, reactions of dehydroxylizing of aluminosilicates and iron hydroxides and reactions of decarbonizing of calcite take place. The removal of coordinated OH^- ions is presumably accompanied by a rearrangement of the crystal lattice of the minerals and formation of intermediary products.

The leading place in the formation of crystallization structures is occupied by the thermodiffusion processes. Thus, the formation of the mullite phase starts in the middle of a drop of feldspar melt. [7]. It can be assumed that aluminum ions shift toward the center of the melt drop under the effect of the concentration difference. The ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ in metakaolinite is equal to 0.5, whereas in melted feldspar it is 0.17. The driving force of these processes is surface energy [6]. Consequently, an increased difference between the chemical potentials on the particle – particle and plastic – film boundaries activates the material transfer.

The process of destruction of metakaolinite is activated due to the presence of amine and carbonic acids contained in molasses, whose polar groups ($-\text{COOH}$) are adsorbed on the argillaceous particles. Free oxides arising as a consequence of thermal destruction of minerals and contained in molasses are incorporated into the metakaolinite lattice, compensate the excessive negative charge, and form an unstable intermediate fine-disperse phase that is a solid solution. This phase serves as the basis for the emergence of activation centers and subsequent recrystallization.

Apparently, the difference in the porcelain structures based on the industrial and the experimental mixtures can be attributed to the activation of the material transfer process due to the introduction of molasses. The proposed strengthening additive accelerates the process of destruction of metakaolinite and the formation of intermediate compounds, i.e., centers of mullite-formation activation.

X-ray phase analysis (Table 1) indicates that the phase composition of porcelain based on the experimental and industrial mixtures subjected to firing at 1350°C is virtually the same: mullite 28%, quartz 17 – 18%, cristobalite around 1%, and vitreous phase 52 – 54%. The IR absorption spectrum of the experimental sample (Fig. 2g) has two absorption maxima of two mullite varieties and weak absorption spectra of quartz and feldspar. Three types of mullite are observed on the spectrum of the sample made from the industrial mixture (Fig. 2f).

The structure of samples fired at 1350°C is typical of the traditional porcelain structure, i.e., is heterogeneous. An electron-microscope study established that the experimental mixture samples have more pores; however, their sizes are small and they are more evenly distributed over the material matrix. This factor, i.e., increased porosity, as a result of reaction between the strengthening additive and the main components of the porcelain mixture, was used as one of the criteria in determining the optimum quantity of the additive to be introduced.

Thus, the phase composition of materials made from the industrial and experimental mixtures subjected to identical thermal treatment (air-dried and fired) is virtually identical. This shows that molasses can be used as an environmentally safe strengthening additive in making porcelain articles based on nontraditional raw materials by single firing.

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